

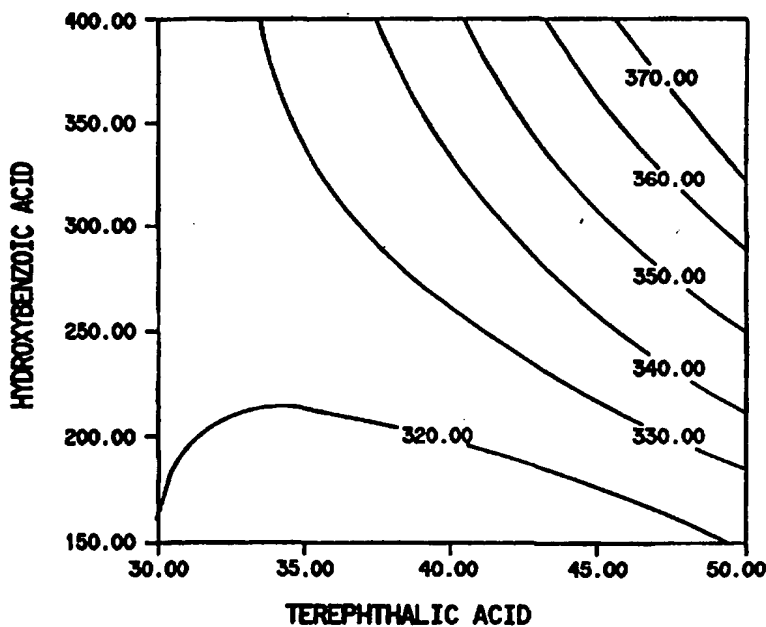
**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C08G 63/60</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/45469</b> <b>(43) International Publication Date:</b> 4 December 1997 (04.12.97)
<b>(21) International Application Number:</b> PCT/US96/07779 <b>(22) International Filing Date:</b> 28 May 1996 (28.05.96) <b>(71) Applicant:</b> E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). <b>(72) Inventors:</b> WAGGONER, Marion, Glen; 36 Sageway, R.D. 3, Hockessin, DE 19707-9803 (US). SAMUELS, Michael, Robert; 5116 New Kent Road, Wilmington, DE 19808-2706 (US). <b>(74) Agent:</b> FORSTNER, James, A.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>With amended claims.</i>

**(54) Title:** LIQUID CRYSTALLINE POLYESTER RESIN**(57) Abstract**

Liquid crystalline polyesters made from hydroquinone, terephthalic acid, 2,6-naphthalene dicarboxylic acid and 4-hydroxybenzoic acid, and having a selected composition range, have melting points of about 350 °C or less, good physical properties, and are readily manufactured. The polymers are useful as molding resins.



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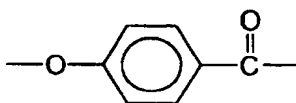
**TITLE****LIQUID CRYSTALLINE POLYESTER RESIN****BACKGROUND OF THE INVENTION**

Described herein are liquid crystalline polyesters made from hydroquinone, terephthalic acid, 2,6-naphthalene dicarboxylic acid and 4-hydroxybenzoic acid which have good physical properties, melting points of about 350°C or less, and can be manufactured rapidly.

Thermotropic liquid crystalline polymers are well known, and are useful as molding resins (for electrical connectors and automotive parts, for example), films, barrier resins, and other uses for thermoplastics. Although these types of polymers are well known, there exists a need for such polymers which have good properties, are easy to prepare, and have relatively low cost.

**SUMMARY OF THE INVENTION**

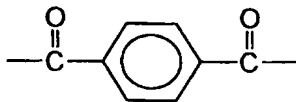
This invention concerns a liquid crystalline polyester consisting essentially of repeat units of the formulas:



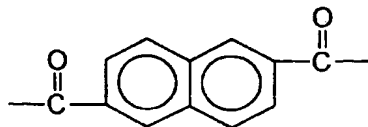
(I)



(II)



(IIIa)



(IIIb)

wherein:

repeat unit (I) constitutes 50 to 63 mole percent of said repeat units;  
repeat unit (II) constitutes 18.5 to 25 mole percent of said repeat units;  
repeat units (IIIa) plus (IIIb) constitute 18.5 to 25 mole percent of said

5 repeat units;

the molar ratio of (IIIa):(IIIb) is 35:65 to 45:55; and

the molar ratio of (II):[(IIIa) + (IIIb)] is about 1.

#### **DETAILS OF THE INVENTION**

The liquid crystalline polyester described herein is a completely aromatic  
10 polyester in which repeat unit (I) is derived from 4-hydroxy benzoic acid (HBA),  
repeat unit (II) is derived from hydroquinone (HQ), repeat unit (IIIa) is derived from  
terephthalic acid (TPA), and repeat unit (IIIb) is derived from 2,6-naphthalene  
dicarboxylic acid (NDA). Those persons skilled in the art will recognize that the total  
molar amount of HQ will be substantially equal to the total combined amount of TPA  
15 and NDA. In preferred polymers repeat unit (I) constitutes 53 to 60 mole percent of  
the polymer repeat units, and repeat unit (II) constitutes 20 to 23.5 mole percent of the  
polymer repeat units and repeat units (IIIa) and (IIIb), when combined constitutes 20  
to 23.5 mole percent of the polymer repeat units.

#### **BRIEF DESCRIPTION OF THE FIGURES**

20 Figure 1 is a contour plot of melting points vs. the two polymer  
compositional variables: the percent HBA [unit (I)] in the polymer; and amount of  
TPA (IIIa) in the ratio of (IIIa):(IIIb) (as described above). Each contour line  
represents a constant value for a melting point, which is shown.

Figure 2 is a contour plot of finishing time (in hours) vs. the two polymer  
25 compositional variables: the percent HBA [unit (I)] in the polymer; and amount of  
TPA (IIIa) in the ratio of (IIIa):(IIIb) (as described above). Each contour line is  
represents a constant value for the finishing time. By finishing time is meant the  
amount of time under full vacuum needed to reach a certain viscosity, as measured by  
torque on the stirrer (see the Examples).

30 Data from Examples 1-8 was used to calculate the contour plots, even  
though not all of the polymers made in these Examples are within the claimed  
composition range. The data were statistically analyzed and calculated using a  
program from SYSTAT, Inc., Evanston, IL, U.S.A. called SYSTAT for Windows,  
Version 5, and using the contour plot routine.

35 It is evident from Figure 1 that the melting points of the polymer  
composition range selected herein are about 350°C or less. This is important to the  
synthesis of high quality polyesters. It has been the experience of the present

inventors that when temperatures much above 350°C are required to make a polyester liquid crystalline polymer, degradation of the starting materials and/or polymer products is markedly increased, thereby leading to undesirable effects such as excessive discoloration of the polyester. To avoid crystallization of the polymer, the polymerization is usually run at or above the melting point of the polymer. Therefore melting points of about 350°C or below are desirable. However, in order to have a high use temperature for the polymer, melting points should also be as high as possible, i.e., in this case close to 350°C. The selected polymer compositions have such melting points, as shown by Figure 1.

For reasons of economy (higher productivity of the polymerization equipment), and to minimize polymer degradation at high temperatures, the finishing period should also be reasonably short. As can be seen from Fig. 2, polymers with about 50 mole percent or more of HBA-derived repeat units surprisingly have relatively short finishing times. While the absolute value of the finishing times will vary according to the quality of the monomers used, the size and configuration of the equipment used, etc., the relative order for the finishing times shown in Fig. 2 should not change in a set of polymerizations in which all other variables are held constant.

Therefore, it has been discovered that a selected compositional range of liquid crystalline polyesters made from HBA, HQ, TPA and NDA has an unexpected combination of good properties, ease of manufacture and less potential polymer degradation during synthesis.

The instant liquid crystalline polyesters can be made by methods known to the artisan for making aromatic polyesters. For instance, the acetate esters (or other low alkyl ester) of the hydroxyl groups in the basic monomers (the 2 hydroxyl groups of the HQ and the one of HBA) may be mixed with the diacids and heated, gradually removing byproduct acetic acid, to eventually form the desired polymer. In a variation of this procedure, the acetates can be formed in situ by adding slightly more than a stoichiometric amount of acetic anhydride to a mixture of all the monomers, heating the mixture to its boiling point, holding for a short time to acetylate the hydroxyl groups, and then performing the polymerization condensation. Alternatively the phenyl esters of the carboxylic acid groups in the monomers may be reacted with the hydroxyl groups, while removing byproduct phenol by distillation. The reactants are usually eventually heated above 300°C under vacuum to achieve a desirable polymer molecular weight.

The polymers disclosed herein may be mixed or compounded with a variety of materials normally mixed with thermoplastics, such as fillers and/or reinforcingers such as glass fiber; glass spheres; flaked glass; carbon fiber; carbon blacks;

and minerals, such as clay; pigments; colorants; stabilizers; other polymers; tougheners; antioxidants; flame retardants; and plasticizers.

### EXAMPLES

#### 5 Examples 1-8

A three-liter glass kettle was used as the reaction vessel. Heat was supplied to the vessel via an electrically heated metal bath composed of bismuth and tin. Agitation was provided by a Cole-Parmer Master Servodyne Unit equipped with a 50:1 gear reducer. Torque (in D.C. millivolts) and RPM were constantly displayed during operation. Vapors boiled from the vessel passed through a one-piece, 2.5 cm O.C. glass column and through a water cooled condenser equipped with a splitter to drain condensed distillate into a 1 liter graduated cylinder. A nitrogen bleed valve was attached to the system to provide a nitrogen blanket prior to the acetylation, polymerization, and distillation steps of the reaction. After most of the distillate had evolved, an additional nitrogen bleed valve was attached to the vacuum-pump side of the system to allow for control of pressure reduction during the partial vacuum stages of synthesis. A Hastalloy\ stirring agitator was placed in the kettle and guided through the kettle top via a Teflon\ bushing equipped with an o-ring for a pressure tight fit.

The entire vessel was then slid into the rubber-surfaced U-shaped lamps and tightened securely. Nitrogen was supplied to the vessel via a safety bubbler and controlled by a needle valve to insure a nitrogen atmosphere. The one-piece glass column, water condenser with splitter, and graduated cylinder were then attached. Stirring was started at 60 rpm until a good visual mix of monomers and acetic anhydride was obtained (approximately 1-2 minutes) then slowed to 50 rpm. At this point the 170°C pre-heated metal bath was raised to cover the reaction portion of the vessel. Acetylation occurred while boiled up acetic acid/anhydride was totally refluxed back to the reaction vessel. The stirring speed was kept at 50 rpm in a clockwise direction (looking down from the top). After 40 minutes of total reflux (to insure total acetylation of the diols), the acetic acid distillate was removed via a splitter on the reflux column, and the set temperature was increased 20 degrees every 20 minutes until the temperature had reached 310°C. After about 20 minutes at 310°C, the set temperature was increased to 370°C to drive off residual acetic acid and maintain a molten resin as it finished under vacuum, which was applied later. After greater than 90% recovery of expected acetic acid, the column, condenser, and graduated cylinder were removed, and a nitrogen line which also was attached to pressure/vacuum reading devices, was installed. The Teflon\ bushing around the stir shaft was fully tightened, and vacuum was slowly applied until the system pressure

reached  $8.4 \times 10^4$  Pa (abs). After 10 minutes at  $8.4 \times 10^4$  Pa (abs), pressure was reduced to about  $6.7 \times 10^4$  Pa (abs) for 10 minutes and decreased by  $1.7 \times 10^4$  Pa every 10 minutes or as behavior of the resin allowed, (*i.e.*, foaming, etc.) until about  $1.7 \times 10^4$  Pa (abs). Pressure was then decreased to  $6.7 \times 10^3$  Pa (abs), then to  $2.4 \times 10^3$  Pa (abs), over 10 minute intervals at which time full vacuum was applied. The system remained under full vacuum (27 to 66 Pa (abs), until the torque reading rose past about 69 millivolts on the Servodyne torquemeter. At this point, the rpm was then decreased to 30 and the torque allowed to rise above 90 millivolts.

Thereafter, the valve to the vacuum pump was closed and the kettle pressurized with nitrogen via the safety bubbler to show when the system had reached atmospheric pressure. The stirring was stopped, the metal bath lowered, and the system dismantled. The hot kettle was set on a cork ring and the top removed. The stir shaft was lifted out and adhering resin was cut away with scissors or scraped off with a putty knife. Any sublimed impurities that adhered to the upper inside portion of the kettle were cleaned off by scraping with a spatula with the kettle on its side to avoid contamination of the remaining resin in the kettle. After this was done, the kettle was placed back into the metal bath to warm up the resin. With a large spatula-type tool the polymer was recovered as the kettle remained in the bath. Typical yield was about 95% when expecting 0.8 kg of polymer.

First heat Differential Scanning Calorimetry (DSC) at a heating rate of  $25^\circ\text{C}/\text{min}$  on as-made polymer was used to measure the melting point ( $T_m$ ) of the polymers made. The  $T_m$  was taken as the peak of the melting endotherm.

The polymer obtained was melt blended in a twin screw extruder with glass fiber to obtain a composition containing 30% by weight of glass fiber. This composition was molded on a single screw injection molding machine with barrel temperatures of about  $330$ - $350^\circ\text{C}$ , to obtain standard test pieces. The tensile properties were measured using the ASTM D-638 procedure, the flexural modulus properties were measured by ASTM D-790, and Heat Deflection Temperature (HDT) was measured by ASTM D-648, at 1.82 MPa load.

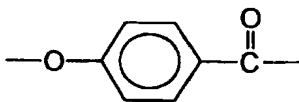
Finishing times and  $T_m$  of the unfilled polyester, and physical properties of the glass fiber filled polyesters are found in Table I.

TABLE I

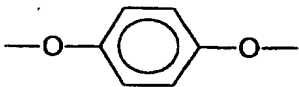
Example No.	Polymer Composition Mole %				T <sub>m</sub> °C	Finish Time hr	Tensile Strength MPa	Tensile Elong. %	Flexural Modulus GPa	Flexural Strength MPa	HDT °C
	HQ	TPA	NDA	HBA							
1	28.6	11.4	17.1	42.9	318	1.58	139	2.0	12.9	190	285
2	16.7	6.7	10.0	66.7	348	0.55	138	2.0	13.0	183	291
3	22.2	8.9	13.3	55.6	328	1.18	142	2.2	12.0	176	283
4	22.2	10.0	12.2	55.6	337	1.17	143	2.0	12.4	181	287
5	18.2	7.3	10.9	63.6	342	0.78	147	2.3	12.5	180	287
6	20.0	7.0	13.0	60.0	327	1.22	143	2.1	12.5	181	286
7	20.0	10.0	10.0	60.0	364	0.77	136	2.4	11.2	163	289
8	20.0	8.0	12.0	60.0	335	1.13	150	2.6	12.2	178	284

**CLAIMS**

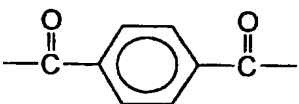
1. A liquid crystalline polyester consisting essentially of repeat units of  
 5 the formulas:



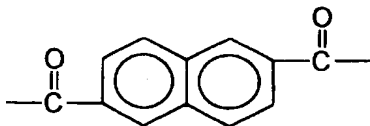
(I)



(II)



(IIIa) and



(IIIb)

wherein:

- repeat unit (I) constitutes 50 to 63 mole percent of said repeat units;  
 20 repeat unit (II) constitutes 18.5 to 25 mole percent of said repeat  
 units;

repeat units (IIIa) plus (IIIb) constitute 18.5 to 25 mole percent of  
 said repeat units;

the molar ratio of (IIIa):(IIIb) is 35:65 to 45:55; and

25 the molar ratio of (II) to [(IIIa) + (IIIb)] is about 1.0.

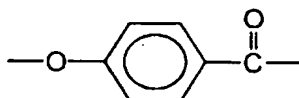
2. The liquid crystalline polyester as recited in Claim 1 wherein repeat  
 unit (I) constitutes 53 to 60 mole percent of said repeat units.

**AMENDED CLAIMS**

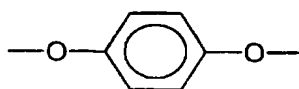
[received by the International Bureau on 3 April 1997 (03.04.97);  
original claims 1 and 2 replaced by new claim 1 (1 page)]

**CLAIMS**

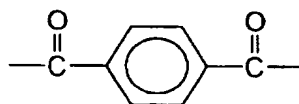
1. A liquid crystalline polyester consisting essentially of repeat units of  
5 the formulas:



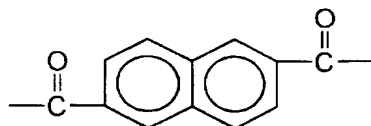
(I)



(II)



(IIIa) and

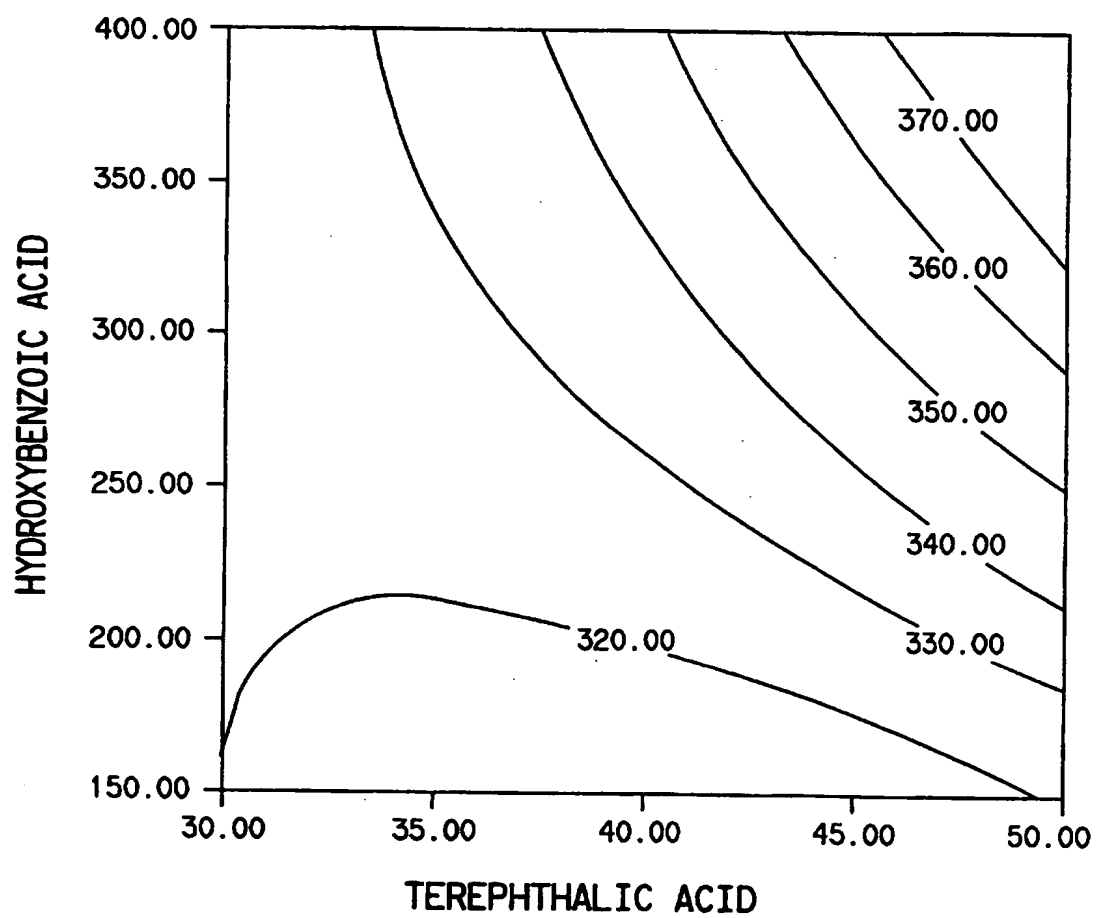


(IIIb)

wherein:

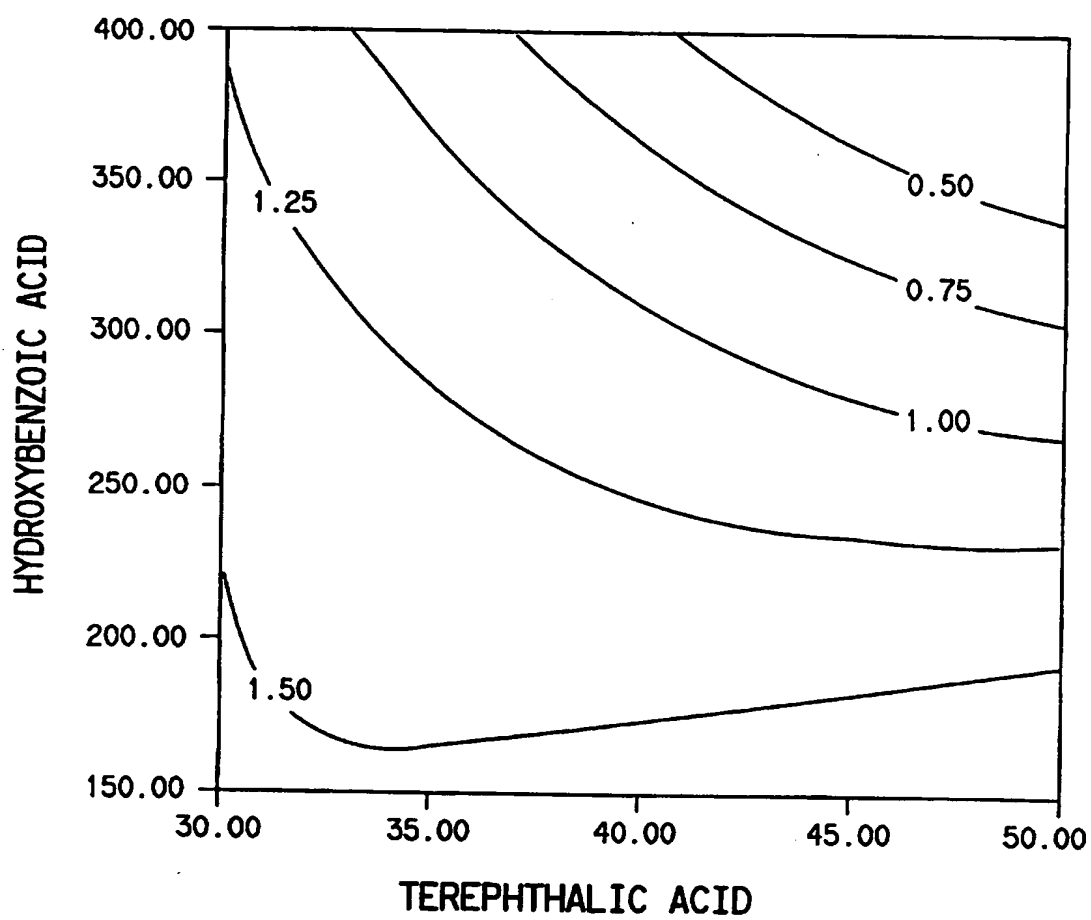
- repeat unit (I) constitutes 53 to 60 mole percent of said repeat units;  
repeat unit (II) constitutes 18.5 to 25 mole percent of said repeat  
units;  
repeat units (IIIa) plus (IIIb) constitute 18.5 to 25 mole percent of said  
repeat units;  
the molar ratio of (IIIa):(IIIb) is 35:65 to 45:55; and  
the molar ratio of (II) to [(IIIa) + (IIIb)] is about 1.0.

FIG. 1



2/2

FIG. 2



SUBSTITUTE SHEET (RULE 26)

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 96/07779

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08G63/60

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 169 933 (JACKSON WINSTON J JR ET AL) 2 October 1979 see column 5, line 35 - line 61; figure 1 ---	1,2
X	MACROMOLECULES, vol. 16, no. 7, 1983, pages 1027-1038, XP002022434 W.J. JACKSON, JR: "Liquid Crystal Polymers" see page 1030; figure 3 ---	1,2
A	EP,A,0 357 207 (EASTMAN KODAK CO) 7 March 1990 see examples 2,5 --- -/--	1,2

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

10 January 1997

Date of mailing of the international search report

11.02.97

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# INTERNATIONAL SEARCH REPORT

International Application No.  
PCI/US 96/07779

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US,A,4 337 191 (FAVSTRITSKY NICOLAI A) 29  June 1982  see column 4, line 6 - line 42  see claim 1  -----</p>	1,2

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/US 96/07779

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4169933	02-10-79	DE-A- 2834537	22-02-79
		FR-A- 2400043	09-03-79
		GB-A, B 2002404	21-02-79
		JP-C- 1480669	10-02-89
		JP-A- 54030290	06-03-79
		JP-B- 63019530	22-04-88
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EP-A-0357207	07-03-90	US-A- 4849499	18-07-89
		CA-A- 1321672	24-08-93
		EP-A- 0426730	15-05-91
		JP-T- 4500081	09-01-92
		WO-A- 9001511	22-02-90
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US-A-4337191	29-06-82	CA-A- 1141083	08-02-83
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